

Adsorption Selective Carbon Membrane the for Separation of O₂/N₂ and C₁-C₄ Hydrocarbon/N₂

Abdul Rahim Jalil, Mohd Ghazali Mohd Nawawi, Norhaslina Mohd Sakri, Nor Zamiha Jusoh
@ Alias

*Department of Chemical Engineering, Faculty of Chemical and Natural Resources Engineering,
Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.*

Abstract

In this study, adsorption selective carbon membranes were developed using cellulose acetate as carbon precursor. The membranes were used for the separation of C₁-C₄ hydrocarbon and O₂/N₂. The carbon membranes were prepared via pyrolysis process using microfiltration ceramic membranes at different temperatures of 300 °C, 325 °C, 350 °C, 400 °C, 450 °C, and 500 °C under nitrogen (N₂) flow rate maintained at 200 ml/min. The membranes were then further subjected to oxidative treatments at the temperatures between 150 °C to 400 °C with an interval of 50 °C. Results showed that the pyrolysis temperature played an important role in determining the morphology of the carbon membranes. As the pyrolysis temperature increased, more pores with smaller diameter were formed. As a result, the permeability of the permeating gases reduced. Results also showed that, for the separation of O₂/N₂ the highest selectivity of 3.92 was obtained using the carbon membrane prepared at 400 °C. The same membrane was then further subjected to an oxidation temperature at 300 °C. The membrane was used for the separation of single and binary gas. For single gas separation, the selectivities for, C₂H₆/N₂, C₃H₈/N₂, and n-C₄H₁₀/N₂ were 2.52, 2.44 and 2.35, respectively. For the binary gas experiment, the selectivities for C₂H₆/N₂, C₃H₆/N₂, and n-C₄H₁₀/N₂ obtained were 3.3, 14.4, and 26.05, respectively.

Keywords: Adsorption, carbon membrane, selectivity, thermosetting polymer

1.0 Introduction

Membranes are becoming more significant in chemical technology and being used in variety of applications in our daily life. Currently there is a growing interest in the development of gas separation membrane based on materials with good chemical and mechanical stability.

The growing significance of membrane and membrane process as efficient tools for laboratory and industrial scale mass separations is based on the several properties, characteristics of all membrane separation process, which make them superior to many conventional mass separation methods [1]. Ideally, membrane for gas separation has higher selectivity and higher permeability, is the most economical gas separation process. However most of the early membrane-based gas separation was limited for commercial applications due to lack of productivity. This is mainly because membrane has to be relatively thick and dense to avoid irregularities on membrane surface that cause dramatic loss in selectivity [2].

Gas flow through microporous material is important to many industrial applications using membrane gas separations. In particular, recent efforts in the oil and gas processing industries

concentrate on the exploitation of carbon membrane. Carbon membrane is also superior to other methods available nowadays such as distillations, adsorption and absorption that is based on energy consumption. This separation has been recognized as a key technology for use by the petrochemical industries [3].

Conventional processes for the separation of certain gases from gaseous mixture are based on the physical properties of various constituent that we want to separate. An example is the removal of hydrogen sulfide from natural gas. This process leaves sulfides as a waste, thus adding the complexity of the whole process. A real application of the complexity of this process is in the refinery itself where a complex unit is design and operated in order to remove the sulfur produced in a safely manner.

In recent years membranes and membrane processes have become industrial products of substantial technical and commercial importance. In fact, a major demand has emerged for the utilization of membrane technology in gas separation applications. Polymeric membrane has been used extensively produced by various researchers and surprisingly results have been achieved. There is a lack in terms of stability of polymeric membrane that cannot be encountered by the conventional polymeric membranes but can be overcome by using carbon membrane. Carbon membrane could withstand harsh operating environments such as high operating pressure and temperature without losing their performances. The use of carbon membrane technology has been focused in the gas separation process in an effort to achieve a higher permeability and selectivity of the process before it could be applied to the industry broadly [4].

There are many different ways to develop carbon membranes for gas separation applications. Ultimately however, it is very critical that the pores of the membrane could be controlled in a reproducible and tailored fashion. By tailoring the pore of the membrane, specific applications could be identified. It has been postulated that the presence of adsorbed molecules forms a barrier to the diffusion of non-adsorbed molecules and hence hinder their transport [5]. Based on this postulated statement, this research work was carried out in order to study the compatibility of the carbon membrane based on cellulose acetate to separate absorbable and non-absorbable gases. Cellulose acetate (CA) was used as the carbon precursor. CA was selected as the membrane material because of its commercial availability, low cost and ease of processing. It has been used for membrane material and relatively inexpensive [6]. Cellulose acetate is also one of few polymers currently being used in commercial gas separations

The main objective of this research is to develop a new kind of adsorption selective carbon membrane instead of molecular sieve carbon membrane. The carbon membrane should be capable of separating gas based on their adsorption characteristics of the gas molecule and the membrane itself.

2.0 Materials and Methods

2.1 Material

Cellulose acetate (CA) was used as the carbon precursor. N,N-dimethylacetamide (DMAc) (boiling point; 165.2^oC) was chosen as a solvent in this research in order to prepare the carbon precursor solution. For cleansing purposes, nitric acid (HNO₃) (boiling point; 122^oC)

and deionized water were used. All chemicals were used as received in reagent grade purities.

2.2 Membrane Preparation

The carbon precursor were prepared by dissolving 20 wt% cellulose acetate in N,N-Dimethylacetamide (DMAc). The solutions were then stirred for 72 hours at ambient air to ensure homogenization of the solution. The solutions then were filtered and allowed to settle for degassing before they were deposited into the porous ceramic membrane.

Dip coating technique was chosen as a method to deposit the carbon precursor. Coating the precursor was done into the inner side of the ceramic support. This was selected for ease of handling and also to avoid cracks that might occur during the development of the membranes. The coating time was set to 15 second. The coated membranes were taken out and cured at controlled temperature using Carbolite furnace (CWF 1100) with heating rate 2 °C/min to targeted temperature of 120 °C and maintained for an isothermal period of 2 hour before allowing the furnace to cool down.

The developed membranes were then subjected to pyrolysis process at 325⁰C, 350⁰C, 400⁰C, 450⁰C and 500⁰C. For oxidation temperature, the membrane was oxidized in the range of 150⁰C to 400⁰C with 50⁰C interval for 0.5 hour. The N₂ flow rate was set to 200 ml/min for the entire pyrolysis procedure.

2.3 Membrane Characterization

Scanning Electron Micrograph (SEM-PHILIPS XL-40) was used to study the morphology of the developed carbon membrane. The permeation tests were done at different operating conditions to study the effects of each operating condition on the selectivity and permeability of the gas.

2.4 Gas Permeation Measurement

Gas permeation measurements were performed in situ using the separation rig set up which was developed for laboratory scale. The ceramic tubular carbon membrane was mounted on to the permeation cell as shown in Figure 1

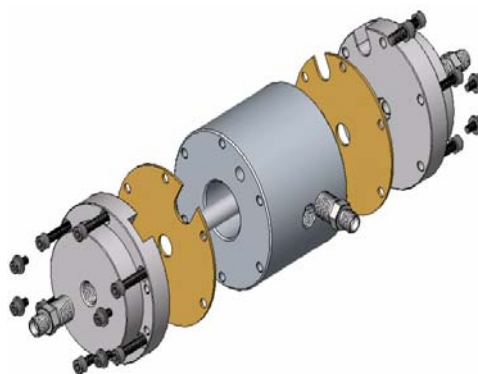


Figure 1 Schematic design of gas permeation cell

Each sample was treated prior to an elevated temperature at 100⁰C for 10 minute to ensure that all H₂O vapor trapped on the carbon surface was completely vaporized. The gas separation apparatus was then purged with nitrogen for 15 minutes prior to any run. Then, high pressure purity gases either single or binary was introduced into the inner space of the modified carbon membrane.

The membrane performance was characterized by the flux of gas component across the membrane, the volumetric gas flow rate, Q is a total volume that passes through the carbon membrane calculated using the equation;

$$Q = \frac{V}{t} \quad (1.1)$$

Where,

Q = volumetric flow rate, cm³/s

V = volume of permeable gas, cm³

t = time, second (s)

Permeability was obtained from the calculation of the volumetric flow rate for the gas. The compositions of permeate and retentate gas were determined by using gas analyzer. Permeant of component i , P_i was calculated using

$$P_i = \frac{J_i}{\Delta p_i} = \frac{Q_i}{A \Delta p_i} \quad (1.2)$$

Where,

P = Permeability constant, cm³ (STP) / cm².s.cmHg

J_i = flux of component i

Q_i = volumetric flow rate of component i at STP, cm³/s

A = surface area of carbonized membrane, cm²

Δp_i = difference of partial pressure of component i between the feed side and the permeate one, cm Hg

The pressure difference of feed side and permeate side was kept constant. The partial pressure of component i at the permeate side was assumed to be 0 kPa because the amount of permeate gas was smaller than the feed gas. The common unit of permeability coefficient is Barrer (1 Barrer = 10⁻¹⁰ cm³(STP).cm/cm².s.cmHg).

The actual thickness of membrane usually is not measurable and cannot be determined explicitly using available methods. Thus, the absolute value of the permeability coefficient remains unknown. Instead the total gas permeation rate was determined as;

$$\left(\frac{P}{l} \right)_i = \frac{Q_i}{A \Delta p_i} \quad (1.3)$$

Where P_i/l is defined as pressure normalized flux or permeability of gas i (permeability coefficient divided by effective skin thickness). Each set of data was determined as an

average of three replicates for consistency of the data. The common unit for measuring the pressure normalized flux of gas applied in membrane is GPU. The equation is;

$$GPU = 1 \times 10^{-6} \frac{cm^3(STP)}{cm^3.s.cmHg} \quad (1.4)$$

The permeability of component i relative to component j is defined as selectivity and can be shown as follow;

$$\alpha_{i/j} = \frac{Perm_i}{Perm_j} \quad (1.5)$$

Gas permeation rate was measured by using pure and mixture of gasses from compressed cylindrical at various pressure gradients. Penetrate gas was introduced without dilution into the feed side. As for that, the feed pressure was controlled at 1, 2 and 3 bar while permeate side were open to vacuum. Experiments were carried out at different temperature (27 °C, 55 °C and 100 °C) with the lower temperature experiment were carried out priority before high temperature experiment. This procedure will prevent the material from being subjected to undue thermal cycling and reduces history dependent behavior from the previous runs.

Permeate stream were collected for a period of time. The analysis of the component exist in permeate stream were carried out using Hewlett Packard Agilent 6890 N. These systems were equipped with thermal conductivity detector (TCD) and four series column. The peaks detected were identified by matching their retention time with Scott Gas Standard (P/N 5080 -8755).

3.0 Results and Discussion

3.1 Membrane Morphology

SEM was employed to study the morphology of the adsorption selective carbon membrane. Figure 2 shows the picture of a surface view of carbon membrane prepared at pyrolysis temperature of 400 °C and oxidation temperature of 300 °C. The picture shows that there were no pores visible even at high magnification of 400X and 500X. Figure 3 shows a cross section of membrane prepared at the same conditions. The absence of pores at very high level of magnification in the Adsorption Selective Carbon Membrane surface layer indicates a dense structure of the homogeneous carbon membrane.

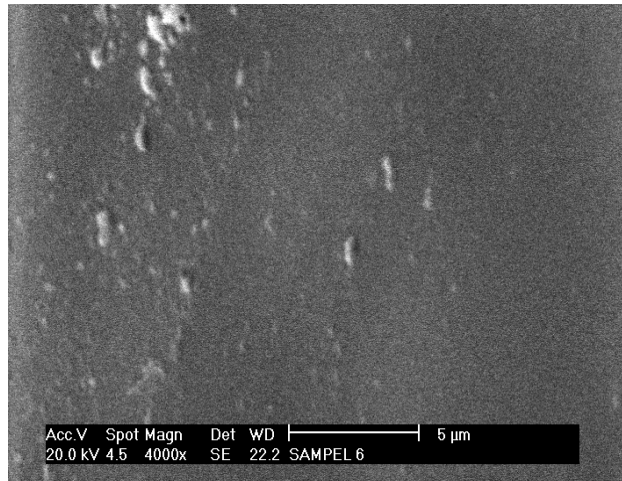


Figure 2 Surface View of Membrane Prepared at Pyrolysis; 400⁰C, Oxidation Temperature; 300⁰C (Magnification 4000X)

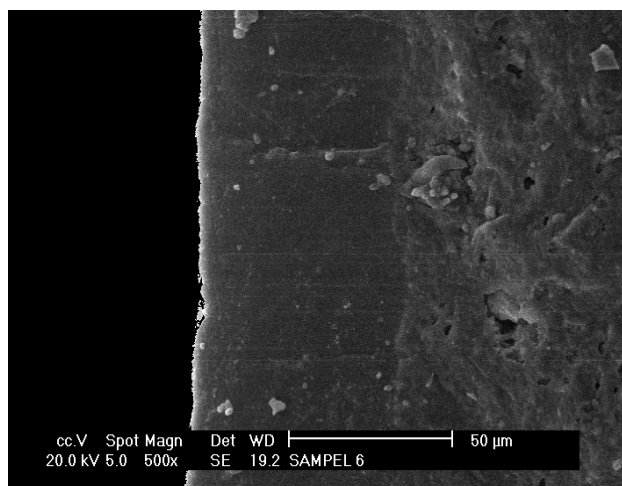


Figure 3: Cross Section View of Membrane Prepared at Pyrolysis; 400⁰C, Oxidation Temperature; 300⁰C (Magnification 500X)

3.2 *Effect of Pyrolysis Temperature on the Carbon Membrane.*

Preparation of adsorption selective carbon membrane was affected by two determining factors which is pyrolysis temperature and oxidation temperature. Pyrolysis temperature plays an important role in the pore formation in carbon membrane. Many parameters are involved during this process such as targeted temperature, heating rate, soaking time and also the type of inert gas used. To minimize the effects of all of these parameters, certain parameters such as soaking time, type and the flow rate of the flowing inert gas were kept constant.

Upon pyrolysis, all the volatile components will be evolved from the precursor membrane and this will create voids or pores in the carbon matrix. The heating rate and targeted pyrolysis temperature will determine the rate of volatilities evolution and subsequently will control the amount and size of the pores present in carbon membrane. The rate of evolution is the key factor in the preparation of the carbon membranes. If the heating rate were too high, it may lead to cracking due to the contraction of the material and or thermal stress [7]. Similar

phenomenon was also observed in this study. We could observe from SEM photograph (Figure 4), there was some deformation at a higher heating rate.

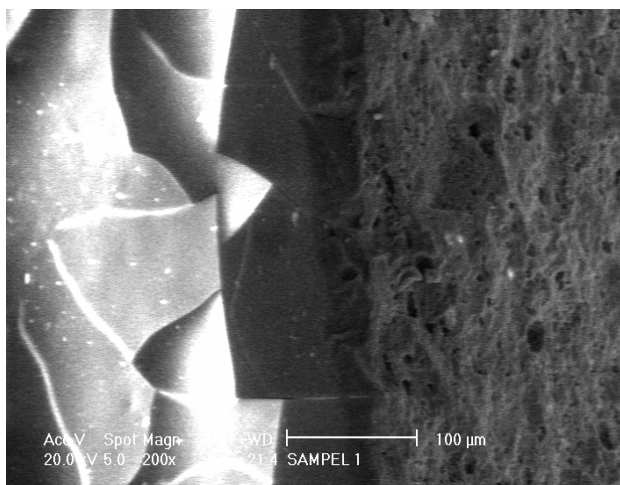


Figure 4 Cross Section View of Membrane Prepared at Pyrolysis; 400 °C, Heating rate 5 °C/min (Magnification 200X).

In fact, some cracks were clearly observed when a heating rate of 5 °C/min was applied during the carbonization of the membrane at a temperature of 400 °C.

Furthermore, the increase in the pyrolysis temperature will affect the gas permeation activity. The effects on the permeation activity of the membrane depend on the size of the pores in carbon membranes. As the pyrolysis temperature increased, we could see clearly there is some deformations of the carbon layer. Thus this lead to the lower permeation of permeating gas due to the collapse of the pore network developed at higher pyrolysis temperature. This phenomena could be seen on the impact of different operating temperature (27°C, 50°C, 100°C) and operating pressure (1 bar, 2 bar, 3 bar) on the permeability of the single and binary gas experiment.

3.3 Permeability Properties of Cellulose Acetate Membranes

3.3.1 Oxygen / Nitrogen Separation

It is widely known that the utilization of both oxygen and nitrogen in our daily life play an important role for the need of pure gas. Pure oxygen is widely used for medical purposes while pure nitrogen is used especially for blanketing perishable fruits and also for shipment of flammable liquids. During this study, the range of pyrolysis temperature was set between 300 °C to 500 °C. Experimental results clearly showed that increasing separation temperature significantly increased the permeability of the flux for the carbon membrane prepared at certain carbonization temperatures. The resultant morphology of carbon membrane had varied with different pyrolysis temperatures.

It was found that the higher the temperature used for the pyrolysis process, the smaller were the pores of the membrane, and thus the smaller the molecule that could permeates through such membrane [8]. As the pyrolysis temperatures were increased, the surface of the carbon membrane developed totally collapsed thus hindering most of the permeating species. As a prove for comparison, we could see from Scanning Electron Micrograph picture that a fine

layer (Figure 2) change to a collapsed structure (Figure 5: Surface View of Membrane prepared at pyrolysis temperature; 500⁰C, Magnification; 4000X).

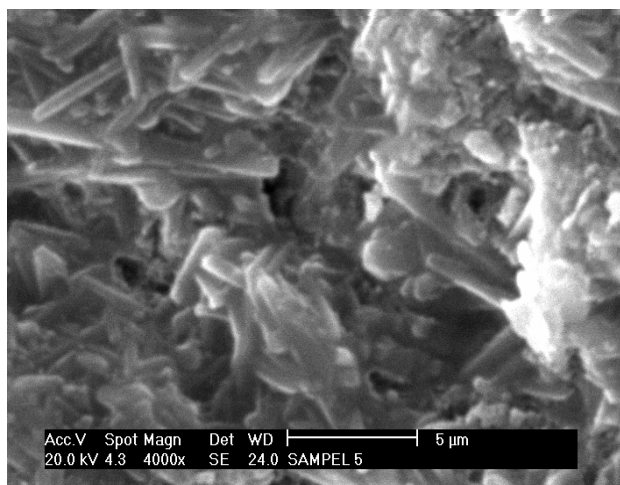


Figure 5 Surface View of Membrane Prepared at Pyrolysis; 500⁰C, Heating rate 2⁰C/min (Magnification 4000X).

In the absence of defects, the selectivity is a function of material properties at the operating conditions [9]. Based on the experimental data collected, the optimum separation temperature for O₂/N₂ separation was achieved at a separation temperature of 400 °C at feed pressure of 1 bar. The value achieved was 3.92. This value almost reach the value for an attractive oxygen separation ranging from 4 to 6 with oxygen permeability 250 Barrer suggested by Puri [10]. This value is also slightly higher than that of gas separation membrane developed by Kulprathipanja [11] who reached oxygen/nitrogen selectivity at 2.99. Kulprathipanja also stated that any selectivity above 3.0 is considered conducive to an excellent separation. The value for oxygen/nitrogen selectivity 2.99 was selected as the target in finding an optimum value for the developed carbon membranes before an oxidative treatment was done. Results has suggested that the optimum temperature was 400 °C.

The feed pressure does not significantly affect the permselectivity properties of the carbon membrane. This study found some contradictions to the other experimental result by previous researchers as at higher pressure level the total permeate should be reduced. The contradiction might due to the difficulty to maintain a constant permeate pressure during the separation of the gases. These findings were also observed by Rauntentbach [12] on his study regarding the impact of operating pressure on hollow fiber membrane used for gas separations. It has been argued whether the total permeability of the gas depends on the feed pressure or the pressure difference across the membrane. However, based on the findings from this study, it can be concluded that the pressure difference play a more important role than the absolute pressure level for the asymmetric permeation properties.

3.3.2 C₁ – C₄ Hydrocarbon / Nitrogen Separation

The main objective of this study is to show the compatibility of the carbon membrane developed in term of separation of hydrocarbon and nitrogen. Analysis of the hydrocarbon gas was carried out at a pressure of 1 bar. In order to determine the optimum oxidation temperature in the range between 150 °C to 400 °C, a systematical pathway was used. Permeation experiments using a high purity nitrogen and methane were carried out and used

as a benchmark property to determine the optimum oxidation temperature. From the experimental results, the permselectivity was increased at lower temperature as a consequence of the increase in the potential barrier of nitrogen due to increasing of hydrocarbon adsorption to the membrane surface. Based on this experimental result, it can be summarized that, in the range of oxidation temperature from 150 °C to 400 °C, the highest value for selectivity were achieved at oxidation temperature equal to 300°C which gave the value for methane and nitrogen permselectivity equal to 2.52. This result will be the basis for the development of adsorption selective carbon membrane using cellulose acetate as the carbon precursor. Analysis was further carried out for the separation of other hydrocarbon gases that is ethane, propane and n-butane at feed pressure equal to 1 bar. The result for analysis are presented in Table 1 for permeation of single gas and Table 2 for permeation of binary mixtures with equal percentage.

Table 1 Separation of single gas (Temperature; 27⁰C, Pressure; 1bar)

Permeability (GPU)		Permselectivity (Hydrocarbon/N ₂)	
Hydrocarbon		N ₂	
CH ₄	: 626.22	248.50	2.52
C ₂ H ₆	: 606.5	248.50	2.44
C ₃ H ₈	: 585.6	248.50	2.35
n-C ₄ H ₁₀	: 405.85	248.50	1.63

Table 2 Separation of binary gas (Temperature; 27⁰C, Pressure; 1bar)

Permeability (GPU)		Selectivity (Hydrocarbon/N ₂)	
Hydrocarbon		N ₂	
C ₂ H ₆	: 208.74	63.25	3.30
C ₃ H ₈	: 167.31	11.62	14.40
n-C ₄ H ₁₀	: 115.95	4.45	26.05

It could be observed from both tables that there are some differences in terms of value of permselectivity and selectivity of the gas been separated. For the permeation of single gas, the value of hydrocarbon is slightly higher than for binary gases experiments. On the other hand the selectivity value for nitrogen decreased as the molecular weight of hydrocarbon increased in the binary gas experiment compared to single gas experiments which are constant. In consequence, the measured (hydrocarbon/N₂) selectivity is larger than the estimated from pure gas experiments. In addition, the selectivity is increased with the increase in molecular weight of hydrocarbon and that means the membranes selectivity increases with the hydrocarbon condensability. This proves that the molecules of the hydrocarbons occupying the pore exist in the membrane surface and partially inhabiting the diffusion on non-absorbable species (N₂). This fact support the statement postulated by Yang [14], which postulated that the presence of adsorbed molecules form a barrier to the diffusion of non-adsorbed molecules, and hence hinder the transport across the membrane. Ash et al [15] also observed that the permeances of weakly adsorbed components are drastically reduced in the presence of strongly adsorbed components. This study also reaches the same

postulate found by other researcher. As a prove we could see that from the experimental result the degree of hindrance of N₂ diffusion increases from methane to butane because the more condensable hydrocarbon is more strongly adsorbed. On the other hand, the adsorption of hydrocarbons on the membrane surface effectively reduces the amount of open void space and hence alters the permeation of nitrogen through the void spaces. The impact of operating temperature was further studied for the separation of single gas.

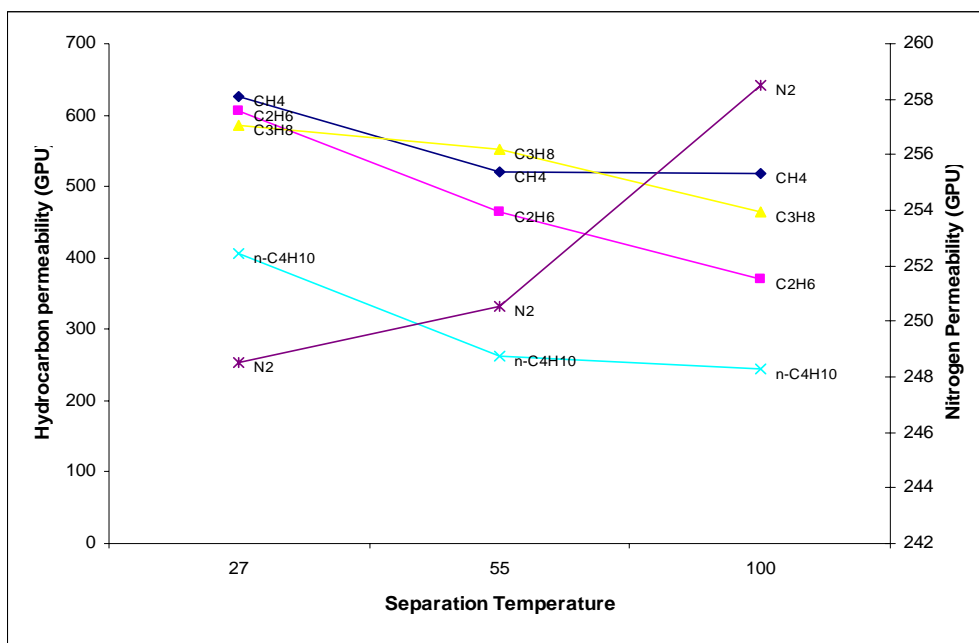


Figure 6 Modification of gas permeability through cellulose acetate derived-carbon membrane with temperature; single gas

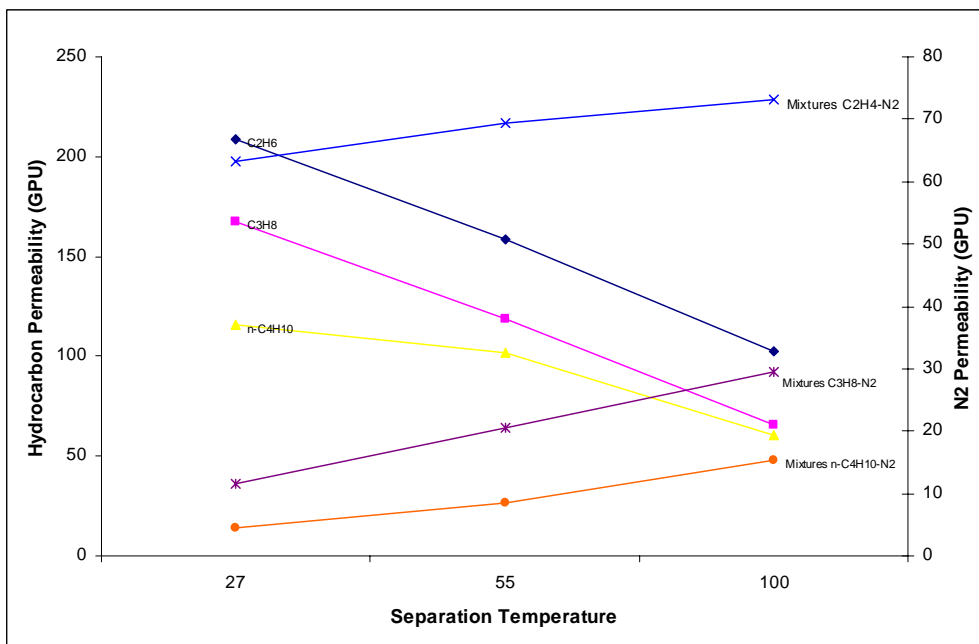


Figure 7 Modification of gas permeability through cellulose acetate derived-carbon membrane with temperature; binary gas mixtures

The effects of hydrocarbon adsorption on the diffusion of nitrogen through the carbon membrane was clearly supported by the experimental data. The presence of hydrocarbon gas, the adsorbing molecules, hindered the permeation of nitrogen gas, the non-adsorbing gas. The effects of the presence of hydrocarbon on the selectivity of the single and binary gases are summarized in Table 1, Table 2, Figure 6 and Figure 7. As could be seen, the magnitude of the hindrance effects of the hydrocarbon on the selectivity of the single gas is significantly higher than on the binary gases. For example, the selectivity of single gas (Table 1) for C_3H_8/N_2 is 2.35 and the selectivity of binary gases for C_3H_8/N_2 (Table 2) is 14.40. In other words, by using binary gases, the selectivity was improved by more than 5 times. Further improvement of the selectivity by using binary gases was obtained for the separation of $n-C_4H_{10}/N_2$; the selectivity for the binary gases improved by more than 15 times compared to the selectivity for the single gas. The increase in the selectivity for the binary gases suggested that the presence of the more adsorbing molecules, which is the hydrocarbon gas, hindered the permeation of the non-adsorbing gas, nitrogen. The selectivity increases when the permeation decreases, vice versa.

The effects of the operating temperature on the hydrocarbon and nitrogen permselectivity were also studied. Results showed that, optimum separation was obtained at lower operating temperature. Experimental results showed that the permeability for the non-adsorbing gas, nitrogen, increased with the increase in the separation temperature. On the other hand, the permeability for the adsorbing gas decreased gradually with the increase in the separation temperature. The same phenomenon was observed for both the single and binary gases separation. Since there is always a trade-off between permeability and selectivity, the selectivity for the nitrogen decreased, while the selectivity for hydrocarbon increased with the increase in the separation temperature.

4.0 Conclusion

Adsorption selective carbon membranes were prepared using ceramic via pyrolysis of cellulose acetate as the carbon precursor. The membranes were tested for the separation of hydrocarbon and nitrogen at different operating temperatures. Major conclusions that can be drawn from this study include:

- i. cellulose acetate is potentially useful for the development of adsorption selective carbon membranes for the separation of hydrocarbon and nitrogen;
- ii. the development of the carbon membranes involved some parameters including selection of polymeric precursor, carbonization conditions and oxidation conditions that affect the separation performance of the membranes;
- iii. the presence of the adsorbing gas hindered the permeation of the non-adsorbing gases; and
- iv. the permselectivity of the carbon membranes for the separation of binary gases is significantly different than that of single gas.

Acknowledgement

The financial support by Ministry of Science, Technology and Environment of Malaysia for funding this research through IRPA project is gratefully acknowledged.

References

- [1] Mohd Ghazali Mohd Nawawi, (1997). *Pervaporation Dehydration of Isopropanol-Water Systems Using Chitosan Membranes*. University of Waterloo. Ph.D. Thesis.
- [2] Geankoplis, C. J. (1993). *Transport Process and Unit Operations*. 3rd Ed. Singapore: Prentice Hall International Editions, New Jersey.
- [3] Katsaros, F. K., Steriotis, T. A., Stubos, A. K., Mitropoulos, A., Kanellopoulos, N.K. and Tennison, S. (1997). High pressure gas permeability of microporous carbon membranes. *Microporous Material*. 8: 171-176.
- [4] Ismail, A. F. and David, L.I.B (2003). Future direction of R&D in carbon membranes for gas separations. *Membrane Technology*. April. :4-8.
- [5] Yang, M., Crittenden, B. D., Perera, S. P., Moueddeb, H. and Dalmon, J. A. (1999). The hindering effect of adsorbed components on the permeation of non-adsorbing component through a microporous silicate membrane: the potential barrier theory. *Journal of Membrane Science*. 156: 1-9.
- [6] Reid, R.C.. and Breton, E. (1959). Water and ion flow across cellulosic membrane. *Journal of Applied Polymer Science*. 1. 133-143.
- [7] Centeno, T. A., Vilas, J. L. and Fuertas, A. B. (2004). Effects of phenolic resin pyrolysis conditions on carbon membrane performance for gas separation. *Journal of Membrane Science*. 228: 45-54.
- [8] Soffer, A., Koresh, J.E. and Saggy, S. (1987). *Separation Device*. (U.S Patent 4,685,940)
- [9] Koros, W.J and Mahajan, R. (2000). Pushing the limits on possibilities on large scale gas separation: which strategies. *Journal of Membrane Science* 175: 181-196.
- [10] Puri, P.S. (1996). Gas separation membranes current status. *La Chimica e Industria*. 78: 815
- [11] Kulprathipanja et al (1988). *Separation of Fluids by Means of Mixed Matrix Membranes*. (U.S Patent 4,740,219)
- [12] Rauntentbach, R., Struck, A., Melin, T., Rooks, M.F.M. Impact of operating pressure on the permeance of hollow fiber gas separation membranes. *Journal of Membrane Science*. 169: 217-223.
- [13] Yang, R.T. (1987). *Gas Separation by Adsorption Process*. London. Imperial College Press.
- [14] Ash, R., Barrer, M.R, Lowson, R.T (1973). Transport of single gases and binary mixtures in microporous carbon membrane. *Journal of Membrane Science*. 1: 17